

STEAM AND ET-DSP COMBINED FOR DNAPL REMEDIATION: FULL-SCALE SITE RESTORATION AT YOUNG-RAINEY STAR CENTER

Gorm Heron (TerraTherm, Inc., Fitchburg, Massachusetts)
Steven Carroll and Hank Sowers (SteamTech Environmental Services,
Bakersfield, California)
Bruce McGee (McMillan-McGee Corporation, Calgary, Alberta)
Randall Juhlin (S.M. Stoller Corporation, Grand Junction, Colorado)
Joe Daniel (S.M. Stoller Corporation, Largo, Florida)
David S. Ingle (U.S. Department of Energy, Largo, Florida)

ABSTRACT: In March of 2003, the United States Department of Energy (DOE) completed a full-scale nonaqueous-phase liquid (NAPL) remediation of Area A of the Northeast Site at the Young-Rainey STAR Center, Largo, Florida. The site was contaminated with approximately 2,300 kg (5,000 lbs) of NAPL constituents such as TCE, *cis*-1,2-DCE, methylene chloride, toluene, and petroleum hydrocarbons.

The site was remediated by SteamTech using a combination of steam-enhanced extraction and electrical resistance heating during operations lasting 4.5 months. After the target volume had been heated to or near boiling temperatures, pressure cycles were used to increase the mass removal rates. Each de-pressurization cycle led to large increases in the vapor phase recovery, until a final phase of diminishing returns was reached.

Post-operational sampling at randomly selected locations showed the concentrations of all contaminants of concern (COC) to be well below the remedial goals. The majority of the groundwater samples were below maximum contaminant level (MCL) for all the contaminants of concern. The overall mass balance showed that about 0.5 kg (1 pound) of VOCs remained in the remedial volume, and showed remedial efficiencies of between 99.85 and 99.99 percent for the four chemicals of concern.

This is the first full-scale demonstration of complete source removal at a DNAPL site. Since the post-operational sampling shows all concentrations to be below or close to groundwater MCLs, the thermal remedy may be satisfactory for site closure without a polishing phase.

INTRODUCTION

In situ thermal remediation is becoming an acceptable technology for restoration of NAPL source zones (Davis, 1997). Heating of sites that contain substantial volumes of both sands and clays requires a combination of heating techniques. Steam has been used to heat the more permeable zones, which are typically sandy layers with relatively low clay and mineral contents. The in situ process using steam injection and aggressive fluids extraction was named steam-enhanced extraction (Udell et al. 1991), and several field demonstrations and full-scale cleanups have been conducted.

Both three-phase and six-phase electrical heating were developed as robust techniques in the 1990s and demonstrated in the field. Laboratory studies demonstrated that thermodynamic changes induced by electrical heating can lead to very effective removal of chlorinated solvents from silts and clays (Heron et al. 1998). Since the late 1990s,

several commercial full-scale implementations of both three- and six-phase heating were completed, with the trade name Electro-Thermal Dynamic Stripping Process (ET-DSP) also used for electrical heating (McGee 2003).

The combination of steam and electrical heating is a patented technology named Dynamic Underground Stripping, and was demonstrated at a gasoline spill that had resulted in LNAPL contamination above and below a rising water table at the Livermore Gas Pad (Newmark 1994; Daily et al. 1995). Since that demonstration, no field-scale implementations of the combined heating approach have been documented to the authors' knowledge.

This paper presents the results of a full-scale remediation for DNAPL-impacted soil and groundwater using steam-enhanced extraction and electrical resistance heating in combination.

FIELD DEMONSTRATION: SITE DESCRIPTION AND OBJECTIVES

The Young-Rainey STAR Center (formerly the DOE Pinellas Plant) operated as a Department of Energy site. In the late 1960s, drums of waste and construction debris were disposed of in a swampy area of the Northeast Site. At this site, two distinct NAPL areas have been identified. This paper describes the remediation of the smaller of the areas, Area A.

Figure 1 shows a schematic of the subsurface geology and the well types used for remediation of Area A. It shows an upper, silty and sandy layer that extends to between

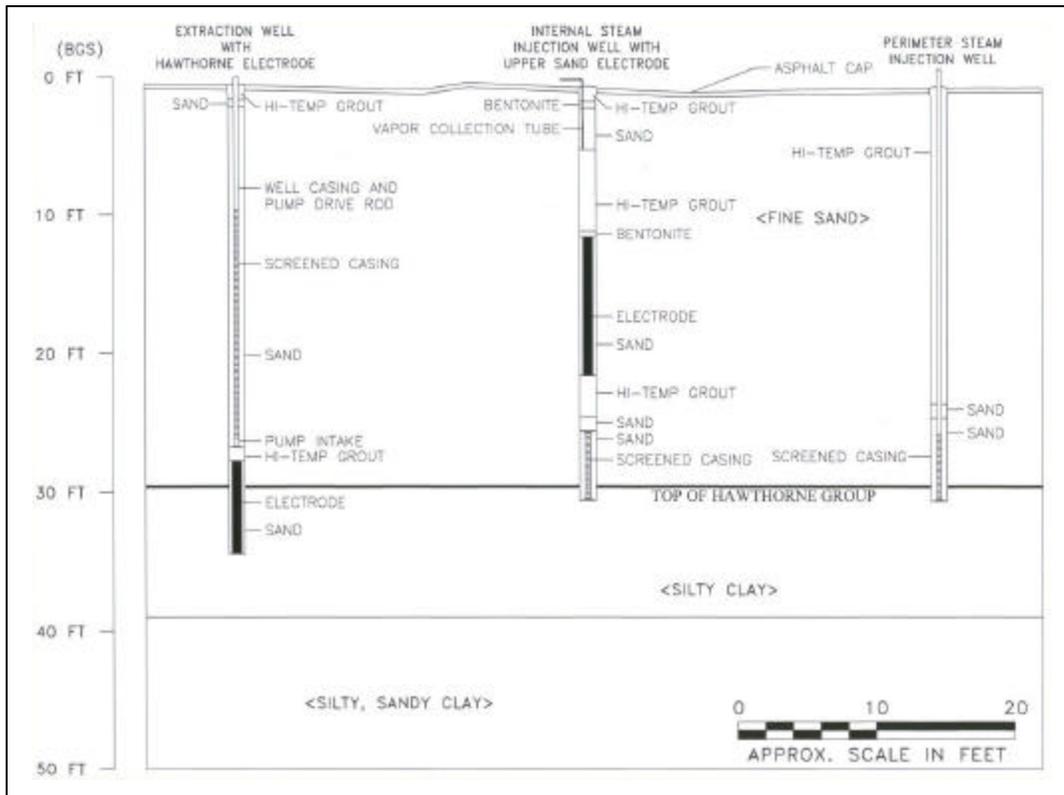


FIGURE 1. Schematic cross-section showing well design features. Target treatment depths are from land surface to 35 ft bgs (5 ft into Hawthorn clay).

8.5 and 10.7 m (28 and 35 ft) depth (the surficial sands). It is underlain by a continuous, silty clay layer, which rests on silty, sandy, and carbonaceous clays at a depth of about 12 m (40 ft). The lower permeability clay layers lying below 10.7 m (35 ft) depth form part of the uppermost Hawthorn Formation.

Groundwater elevations vary between 3 and 4.5 m (10 and 15 ft) above mean sea level at the site, corresponding to depths between 0.3 to 2 m (1 and 6 ft) below grade. The groundwater level is strongly influenced by rainfall, with rapid rises of several feet observed following storm events. The unconfined surficial sand and silt aquifer has hydraulic conductivity in the 10^{-4} to 10^{-3} cm/sec range, corresponding to about 0.1 to 1 darcy intrinsic permeability. The Hawthorn clays and silts are of low permeability, with hydraulic conductivity in the 10^{-8} to 10^{-6} cm/sec range. The Hawthorn Formation clay forms a laterally extensive aquitard at the Northeast Site.

The buried waste contained a wide range of synthetic chemicals, including oils, solvents, resins, and solids. Both DNAPL and LNAPL were positively identified, as they accumulated in on-site wells. The contaminants of concern selected for this site are listed in Table 1. The dominant individual chemicals are TCE, toluene, *cis*-1,2-DCE, and methylene chloride. Petroleum range organics was identified as a parameter of concern for the soils. Table 1 shows the numeric standards established for Area A remediation. These concentrations were determined by DOE to represent levels below which NAPL should not persist in the subsurface.

TABLE 1. Numeric goals for soil and water samples collected post-remediation.

Chemical	Groundwater Cleanup Goal (µg/L)	Soil Cleanup Goal (µg/kg)
Trichloroethene	11,000	20,400
Cis-1,2-Dichloroethene	50,000	71,000
Methylene Chloride	20,000	227,000
Toluene	5,500	15,000
TPH (FL-PRO)*	50,000	2,500,000

*Total Petroleum Hydrocarbons (Florida Petroleum Range Organics)

The distribution of the NAPL and dissolved contaminants was assessed by intensive soil and groundwater sampling. An approach was adapted to delineate the outer boundaries of the treatment volume, horizontally and vertically. It was then assumed that NAPL and contaminants could exist anywhere inside the volume defined, and that thermal remediation should address the entire volume. The resulting treatment area is shown on Figure 2. The treatment depth was defined from land surface to a depth of 1.5 m (5 ft) into the Hawthorn Group, representing a total depth of approximately 10.7 m (35 ft). The treatment area was 930 m² (10,000 ft²) and the treatment volume was 9,930 m³ (12,960 yd³). After thermal remediation, a statistically valid sampling and analysis approach was used to determine whether the numeric goals listed in Table 1 were met.

Sampling and monitoring approaches, as well as the full data set for this remediation, were published in the final report (U.S. DOE, 2003). The remedial activities were conducted by SteamTech Environmental Services, assisted by their subcontractors

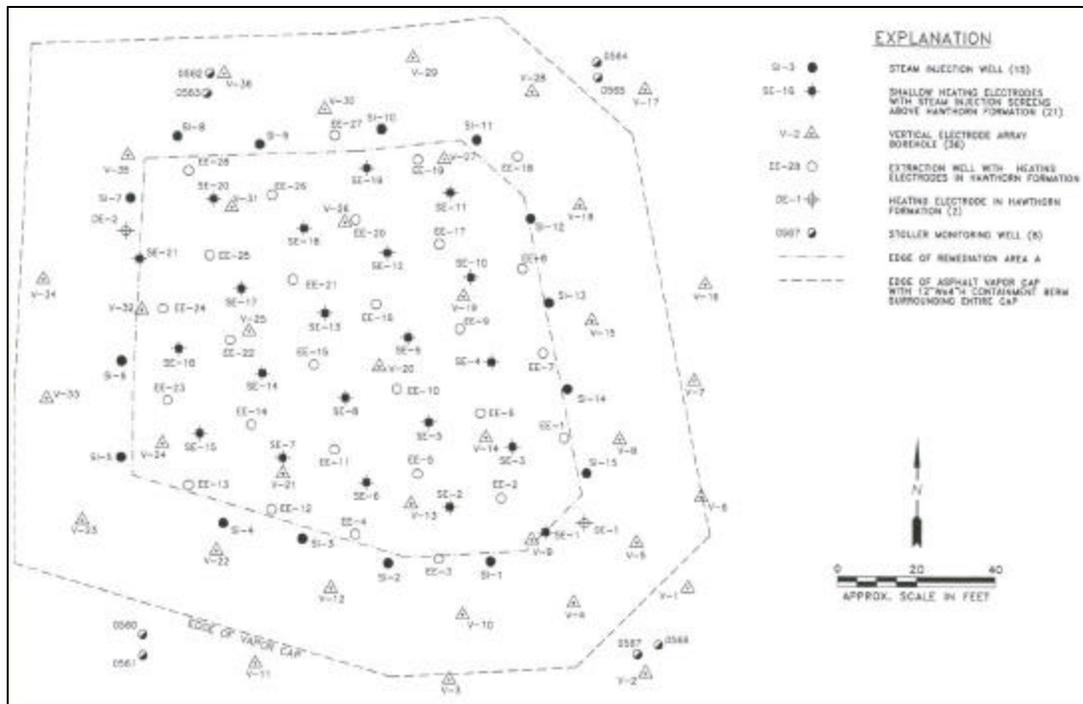


FIGURE 2. Area A at Young-Rainey STAR Center with well locations.

McMillan-McGee Corporation, Geo Consultants, and PPM Co., under oversight by the DOE contractor S.M.Stoller Corporation.

RESULTS AND DISCUSSION

The field operations lasted 4.5 months, and followed a strategy where contaminant spreading was minimized, and recovery was maximized (SteamTech, 2002d):

1. Hydraulic and pneumatic control was established by liquid and vapor extraction. This was achieved after 3 days of continuous extraction on October 3, 2002.
2. Heating of the perimeter and bottom of the treatment volume, while maintaining hydraulic control. Electrical resistance heating was used to heat the upper 1.5 m (5 ft) of the Hawthorn clay, and a combination of electrical resistance heating and steam injection was used to heat the perimeter of Area A. Acceptable heating was achieved on November 6, 2002 after 33 days of heating.
3. Heating of the entire Area A to target temperature, using steam injection and electrical resistance heating in combination, while maintaining hydraulic and pneumatic control. This was achieved on November 15, 2002 after a total of 42 days of heating, when the average temperature inside Area A had reached 84°C, with the zone below 3 m (10 ft) depth generally above 100°C.
4. Pressure cycling and mass removal optimization phase. The pressure cycling was performed by varying the steam injection rates and the electrical power delivery, while maintaining a constant extraction rate. Mass recovery was high at times of depressurization and during times of heating of sub-areas that had remained cool

previously. This phase lasted for 60 days, until the end of heating on February 17, 2003, when diminishing returns were achieved.

5. Cool-down and polishing, involving continued vapor and liquid extraction combined with air and cold water injection. This active cooling lasted 7 days, and was completed on March 24, 2003.

Figure 3 shows the cumulative water and energy balances for the operations period. Overall, the site was heated to an average temperature of 110°C (confirmed by

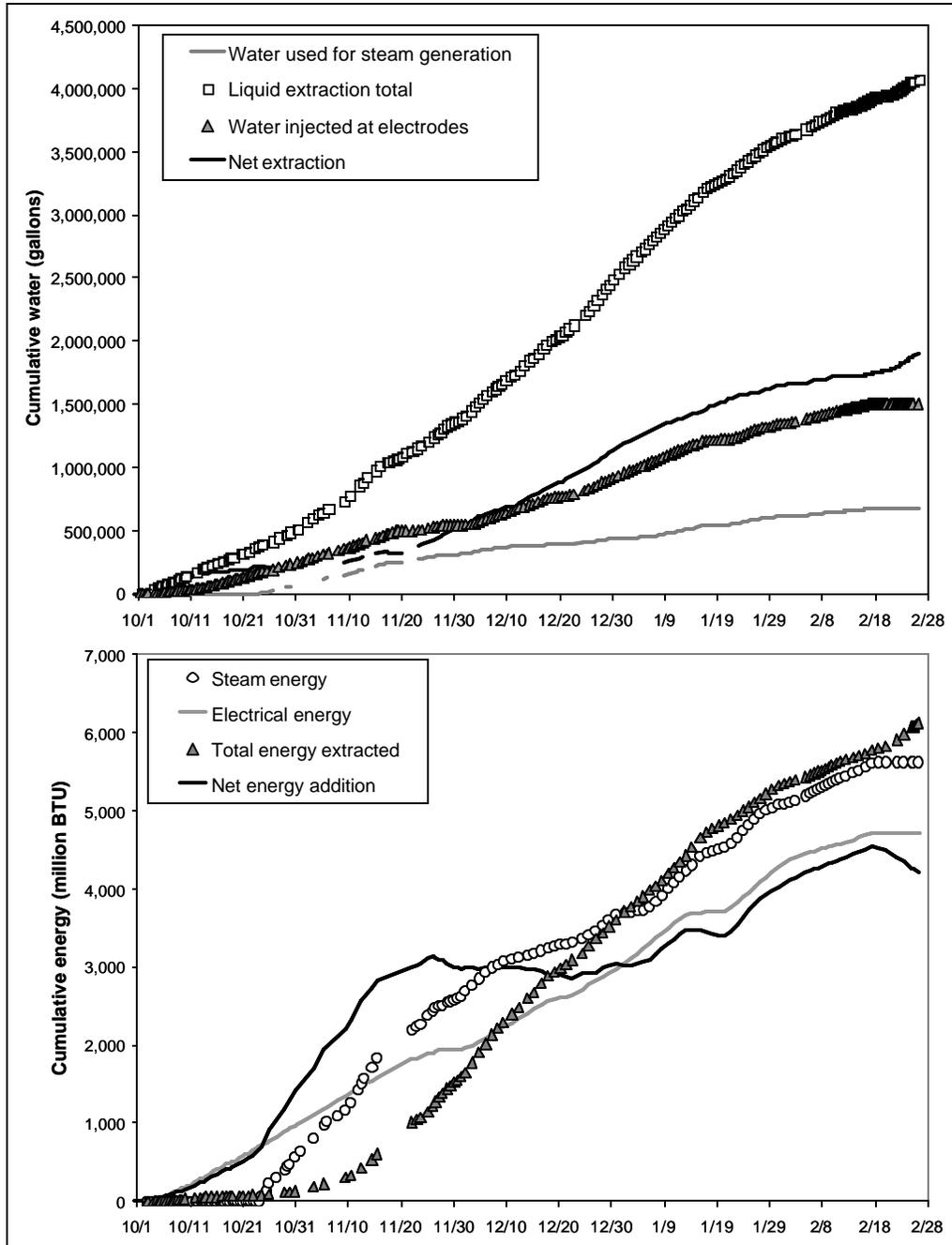


FIGURE 3. Water and energy balances for the 4.5 months of operation.

thermocouple measurements at 36 vertical profiles), while hydraulic control was maintained, and contaminant spreading avoided (confirmed by frequent groundwater sampling from eight monitoring wells surrounding Area A).

Figure 4 shows the results of vapor screening using a PID instrument, along with a rough mass removal estimate based on the PID results. Note that the recovery of VOCs was negligible until early November, when the extracted fluids started to heat up. The VOC removal occurred in large spikes, typically following the decompression phase of the induced pressure cycles. The pressure cycles were performed by adjusting the steam rate up and down, with de-pressurization events following each reduction in the injection rate.

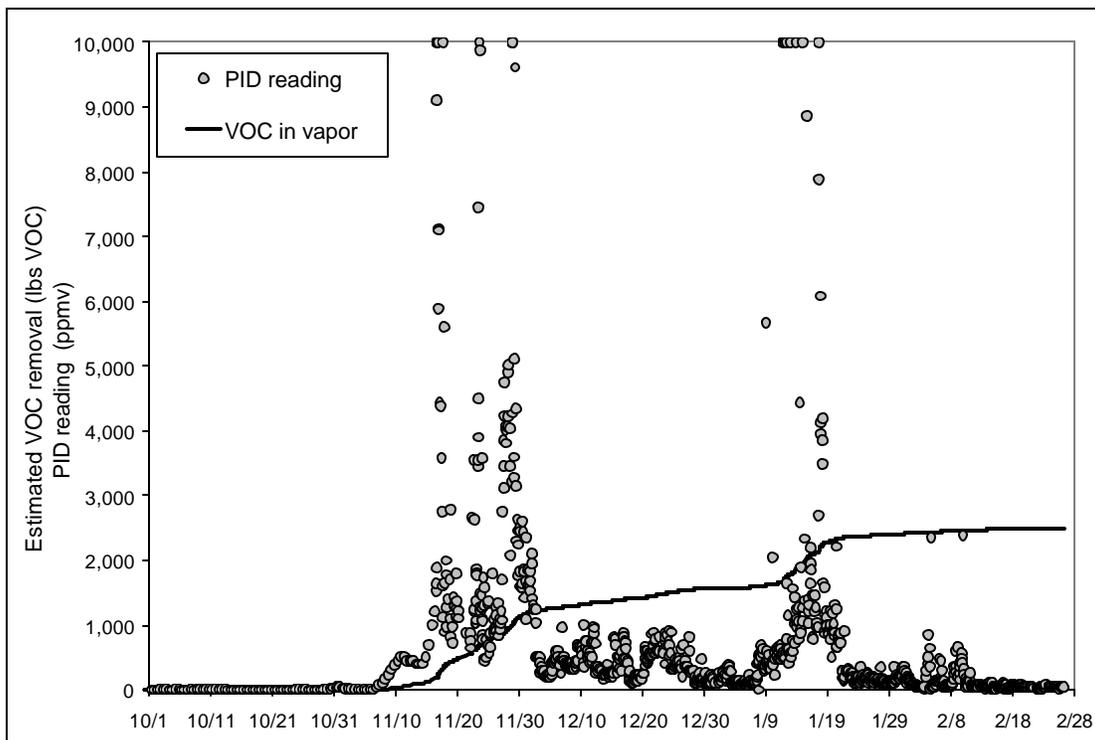


FIGURE 4. PID screening results on the untreated vapor, and estimate of cumulative VOC removal.

In order to examine the progress of the remediation during operations, a total of nine borings were advanced for interim soil samples. The samples showed several high PID readings, and laboratory analysis confirmed that TCE and Toluene soil concentrations exceeded the cleanup levels in a total of four samples. The areas of high concentration in the soil coincided with the location of a resin layer observed during drilling. The resin layer was approximately 0.3 m (1 ft) thick and located 2 m (6 ft) below the surface. A sample of the resin material was analyzed and found to contain high concentrations of methylene chloride and TCE.

To increase the remedial efficacy in this area, six additional shallow screens for steam and air injection or vapor extraction were installed, and used to deliver steam and air to the areas that apparently had been stagnant, and that had resisted remediation. This led to an increase in the mass flux from the subsurface, and the concentrations of COCs

in the nearby extraction wells increased for a short time, then appeared to decrease. During cool-down, air was injected into the shallow screens in order to enhance volatilization, and prevent COCs from condensing in the subsurface.

Post-operation soil sampling was carried out in 20 confirmatory borings, of which 16 were at locations selected by random number generation laid out on a regular grid. All post-operational soil contaminant concentrations were substantially below NAPL remediation goals. Chlorinated VOC concentrations nowhere exceeded 1% of the remediation goals, while toluene and FL-petroleum range organics nowhere exceeded 20% of the remediation goals.

Post-operation groundwater sampling was carried out three times in the 24 confirmatory wells (16 wells inside Area A, eight outside). Samples were collected approximately 4, 8, and 26 weeks after cessation of operation. All confirmatory groundwater samples were below target concentrations, typically being <1% of target NAPL remediation levels and nowhere exceeding 24% of target levels. Groundwater COC concentrations were also below MCL in most of the confirmatory wells.

Based on the sampling of soils before and after the remediation, treatment efficiencies were calculated for the contaminants (Table 2). The total estimate for the mass of VOC left after the remediation is approximately 0.5 kg (1 lb). For all the volatile COCs, the average treatment efficiency for VOCs is around 99.9 %. For TPH, a treatment efficiency of 61% was estimated. Despite the modest removal efficiency, all post-operational samples were below the remediation goals.

TABLE 2. COC treatment efficiency based on mass estimates from soil sampling before and after treatment.

	FL-PRO*	Trichloroethene	Toluene	Methylene Chloride	Cis-1,2-Dichloroethene
Mass before operation (lbs)	2,961	1,008	801	308	128
Mass after operations (lbs)	1,159	0.14	0.89	0.03	0.19
Removal efficiency (%)	60.86	99.99	99.89	99.99	99.85

* Total Petroleum Hydrocarbons (Florida Petroleum Range Organics)

The remedial mechanisms identified or believed to have contributed to the successful removal of the contaminants were (1) vaporization and stripping of VOCs when the subsurface temperatures increased, (2) in situ boiling induced by pressure cycling operations and boiling caused by the electrical heating, (3) hydrolysis of methylene chloride in the heated groundwater, (4) flushing of VOCs by air injection along with the steam, leading to convection from injection to vapor extraction wells, and (5) in situ degradation by biological and chemical reactions (undocumented).

CONCLUSIONS

This is the first full-scale remediation of a DNAPL site by a combination of steam-enhanced extraction and electrical heating. Using steam to deliver energy to the permeable zones, and electrical heating to heat low-permeability zones, can lead to very effective and uniform heating. More importantly, by focusing the heating at the treatment zone perimeter and bottom first, heated barriers can be created around the DNAPL-containing

volume. This can effectively minimize the risk of contaminant spreading, both horizontally and vertically.

This study showed the importance of pressure cycling for accelerating mass removal and shortening the operational time. During the induced pressure cycles, mass removal rates were many times higher than during constant injection and extraction of steam and electrical power. This phenomenon has been well published for 12 years (Udell et al. 1991, Udell 1996), but apparently has not been used effectively in several recent steam projects. The data presented here shows that, without any extra expense, it is possible to increase the treatment efficacy and reduce the operations time simply by temporarily reducing the steam injection rates.

By the removal of about 1,200 kg (2,500 lbs) of volatile contaminants in 4.5 months, soil and groundwater concentrations were lowered to concentrations believed to be at least 100 times lower than levels that would allow DNAPL to exist. By such effective remediation, estimated at an average mass removal efficacy of 99.9% for the volatile contaminants, polishing steps may not be necessary.

ACKNOWLEDGEMENT

The lead author Dr. Gorm Heron was an employee of SteamTech Environmental Services during the implementation of this project. Many thanks to the entire project team for excellence and dedication throughout.

REFERENCES

- Daily, W.D., A.L. Ramirez, R.L. Newmark, K.S. Udell, H.M. Buettner, and R.D. Aines. 1995. *Dynamic Underground Stripping: Steam and electric heating for in situ decontamination of soils and groundwater*. US Patent # 5,449,251.
- Davis, E.L. 1997. *How heat can accelerate in situ soil and aquifer remediation: important chemical properties and guidance on choosing the appropriate technique*. U.S. EPA Issue paper EPA/540/S-97/502.
- Heron, G., M. van Zutphen, M.; T.H. Christensen, and C.G. Enfield. 1998. *Soil heating for enhanced remediation of chlorinated solvents: A laboratory study on resistive heating and vapor extraction in a silty, low-permeable soil contaminated with trichloroethylene*. Environmental Science and Technology, 32 (10), 1474-1481.
- McGee, B.C.W. 2003. *Electro-Thermal Dynamic Stripping Process for in situ remediation under an occupied apartment building*. Remediation, Summer: 67-79.
- Newmark, R.L. (ed.) 1994. *Demonstration of Dynamic Underground Stripping at the LLNL Gasoline Spill Site*. Final Report UCRL-ID-116964, Vol. 1-4. Lawrence Livermore National Laboratory, Livermore, California.
- Udell, K.S., N. Sitar, J.R. Hunt, and L.D. Stewart. 1991. *Process for In Situ Decontamination of Subsurface Soil and Groundwater*. United States Patent # 5,018,576.
- Udell, K.S. 1996. *Heat and mass transfer in clean-up of underground toxic wastes*. In Annual Reviews of Heat Transfer, Vol. 7, Chang-Lin Tien, Ed.; Begell House, Inc.: New York, Wallingford, UK, pp. 333-405.
- US DOE (2003). Pinellas Environmental Restoration Project. Northeast Site Area A NAPL Remediation Final Report. Young - Rainey STAR Center. U.S. Department of Energy, Grand Junction Office, Grand Junction, Colorado. September.